

Photoexcitations in disubstituted acetylene polymers

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Abstract

We have used a variety of optical techniques to study the photoexcitations dynamics in several disubstituted acetylene polymer thin films. We found that although these polymers have a degenerate ground state, as determined by iodine doping and C₆₀ photodoping, they show strong photoluminescence (PL) in the blue/green spectral range with high quantum efficiency (QE) in thin films. The cw photo modulation spectrum contains a single photoinduced absorption (PA) band at 1.7 eV with monomolecular recombination kinetics with a lifetime of 25 ms. PA detected magnetic resonance (PADMR) shows that this PA band is related to spin 1/2 excitations, which therefore identifies it as due to neutral soliton antisoliton pairs (S° , \bar{S}°), similar to the 1.35 eV PA band in t-(CH)_x. No triplet PADMR signal was observed and we therefore conclude that triplet excitations are unstable in disubstituted acetylene polymers, even though singlet excitons are relatively stable. We consider therefore a possible S⁰ photogeneration mechanism via singlet to triplet intersystem crossing, followed by triplet exciton decomposition into \bar{S}° S⁰ pairs. Also we detected polarons in a degenerate ground state polymer for the first time.

Keywords: trans-Polyacetylene, luminescence, electron-electron interactions

1. Introduction

A novel luminescent π -conjugated polymer, disubstituted trans-polyacetylene, puts new light on the understanding of photo physics in degenerate-ground-state polymers. Two different disubstituted acetylene polymers have been investigated in this study (Table 1).

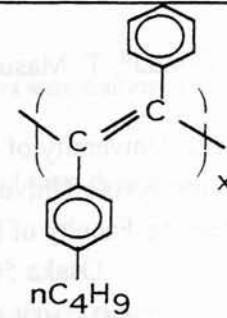
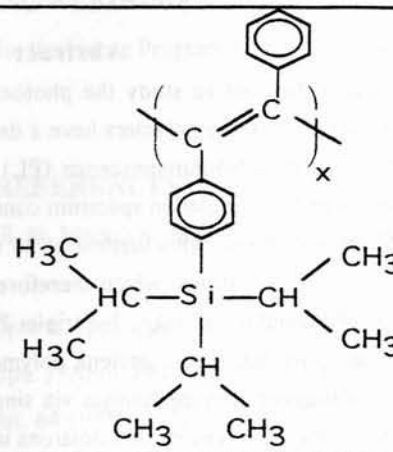
Unsubstituted trans-polyacetylene (t-PA) is nonluminescent despite a weak emission resulting from the optically forbidden decay of the lowest lying 2A_g exciton [1, 2]. Many of the properties of unsubstituted t-PA have been assigned to its degenerate ground state structure, which makes it possible to have stable soliton excitations [3, 4].

The existence of excitons in t-PA has been a matter of controversy: The fact that t-PA has a degenerate ground state and does not have photoluminescence (PL) whereas cis-PA has a nondegenerate ground state and a relatively strong PL, lead some groups to the conclusion that excitons can only be stable in nondegenerate ground state π -conjugated polymers. In these polymers, excitons are unstable towards dissociation into solitons, which move quickly apart from each other due to their repulsive interaction. The fact that t-PA exhibits photocurrent and cis-PA does not, supported this model [3].

Other groups acknowledge the existence of stable excitons even in t-PA. Takimoto et al. [5] performed calculations on the excitation decay kinetics in t-PA, assuming a model which involves an optically allowed exciton (1B_u) and an optically forbidden (2A_g) exciton at an energy below the energy of the 1B_u. Most of the decay of the 1B_u state happens due to relaxation into the optically forbidden (2A_g) exciton and thus the material is nonluminescent. The 2A_g state in turn

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Table 1: disubstituted polyacetylene polymers

<p>Disubstituted Polyacetylene (n-Butyl) PDPA-nBu</p>	
<p>Disubstituted Polyacetylene (Silicon) PDPA-Si(iPr)₃</p>	

decays into a neutral soliton - antisoliton pair. The photocurrent in t-PA can be explained in this model by the polarization current of excitons (fast component) and by polaron excitations (long lived component) [6], but the polaron PA bands have not yet been found directly.

The processes following photoexcitation in this polymer can be summarized as follows. t-PA may support charged and neutral solitons, and polarons. Furthermore, neutral solitons can be generated as the result of defect centers and cross links in the polymer bulk [7]. These trapped solitons can either be charged due to chemical doping [8], or in form of soliton antisoliton pairs due to absorption of a photon [9].

A defect center of high electron affinity can also act similar to a C₆₀-dopant. Upon encounter with a 1B_u exciton, the defect center gets negatively charged and a positive polaron remains [10]. Two polarons of the same charge and opposite spin react to form a charged soliton-antisoliton pair through the intermediate generation of an unstable bipolaron [4, 7].



Among the variety of possible photoexcitations in t-PA, other processes have been proposed [11]: A polaron reacts with a neutral soliton to form a charge soliton:



Two charged solitons combine to neutral solitons or annihilate:



As well as neutral solitons can annihilate:



The same processes should also be seen in samples of disubstituted PA. In the following section we will confirm the existence of solitons and polarons in disubstituted PDPA and analyze their various decay processes in the disubstituted acetylene polymer PDPA-nBu. In addition, we show that PDPA-nBu is luminescent polymer that has a degenerate ground state but at the same time exhibits a strong PL. This finding has important consequences for the understanding of exciton dynamics in conducting polymers and stresses the significance of electron-electron interactions in model Hamiltonians of conducting polymers.

2. Experimental techniques

Various optical techniques have been used to determine the electronic structure of PDPA. Electroabsorption (EA) measures the change in absorption due to the application of an electric field. The analysis of signal is based on a $\chi^{(3)}$ process and allows to determine the excitonic levels and their strongly coupled vibrations. Experimental setup and analysis of EA spectroscopy are described elsewhere in more detail [12, 13]. Electric fields in the order of 10^5 V/cm and sample temperatures of 80K were used in this study.

Photoinduced absorption (PA) spectroscopy measures the change in absorption of a infrared probe beam due to pumping of the material with a strong light beam of photon energies above the absorption edge. In this study, the 0.1 mW of the UV lines of an Ar⁺ laser were mechanically chopped at 400 Hz to periodically pump the material. The pump induces excitation which are detected with the probe beam. A more complete description of the experimental technique and the analysis of the spectra is given by Vardeny et al. [14]. As probe a tungsten lamp was used and the signal was spectrally resolved using a monochromator and infrared filters. Spectra were taken at 80 and 300 K.

Photoinduced absorption detected magnetic resonance (PADMR) and Photoluminescence detected magnetic resonance (PLDMR) measure the change in PA and PL respectively due to magnetic resonance. The spectra were taken at 10K using a microwave frequency of 3 Ghz and magnetic fields at around 500 G and at around 1000 G. The experimental setup is described elsewhere [14-16]. The measurements allow to characterize the spin quantum number of PA and PL active excitations. Careful analysis of PADMR also allows to determine the excitation kinetics.

Doping experiments using dopants with high electro negativity such as iodine are described and analyzed ample in literature[17-19]. A list of all relevant publications would extend beyond the frame of this manuscript. Also the analysis of C₆₀ doping can be found ample in the literature [20-22]

3. Effects of sidegroup substitution

The onset of the absorption indicates the energy of the $1B_u$ exciton. This energy can be determined much more precisely using the first prominent zero crossing of the EA spectrum. Figure 1 shows EA spectra of (a) t-PA, (b) mono substituted t-PA (s-PA), and (c) disubstituted trans-PA (PDPA-Si). EA model calculations have been performed on t-PA and

s-PA [23]. The energy of the $1B_u$ state was calculated to be 1.43 eV and 1.54 eV for long and short conjugation length contributions in t-PA. (A bimodal conjugation length distribution was found by Mulazzi [24] and confirmed in that work) and 1.98 eV in s-PA. Even though the EA of disubstituted PA was not fitted, the data shows that the energy level of the $1B_u$ exciton is approximately at 2.8 eV. The EA spectra of the three polymers show that the optical gap increases with substitution. The result of structural effects such as mechanical strain on the polymer backbone due to large sidegroups is not yet well understood. We can speculate that the steric action plays an important role in the physics of substituted PA's. As a result of the limited space for the large sidegroups, an alternating torsion of the repeat units might occur. This would add to the effect of dimerization and reduce the overlap of the π -orbitals. This contribution of a mechanical effect may increase the bandgap of substituted and disubstituted PAs. As a result of these additional interactions, the relative effect of electron-electron interactions as compared to Peierls and mechanical effects gets smaller in substituted PA's.

Independently Mazumdar et al. using a Peierls Hubbard model [25], and Hirsch et al. using Monte Carlo simulations [26] calculated that electron-electron interactions can enhance the bond alternation. An increase in electron-electron interaction lowers the $2A_g$ state as compared to the $1B_u$ state [27]. In non interacting models, the $2A_g$ state is above the $1B_u$ [28]. PDPA-nBu is luminescent. That this is an indication that due to relatively smaller electron-electron interaction the $2A_g$ state is above the $1B_u$ state in this material and the luminescence is not due to topological effects such as ground state degeneracy or nondegeneracy, will be shown in the following.

4. The luminescence

PDPA-nBu and PDPA-Si exhibit a strong luminescence in green and blue respectively, even in thin films with high quantum efficiencies. However, doping experiments show that 3% C_{60} by weight reduces the luminescence by a factor of 10 and decreases the lifetime of the excitation significantly. This indicates a quenching of excitons due to transfer of an electron to the C_{60} molecule. The luminescence was also used to perform photoluminescence detected magnetic resonance (PLDMR). Figure 2-(a) shows PLDMR data of a PDPA-nBu film on a sapphire substrate. The sample shows magnetic resonance at 1006 G due to spin-1/2 excitations. A quenching of spin-1/2 excitations due to magnetic resonance increases the ground state population. Thus the radiative decay of the $1B_u$ exciton to the ground state is enhanced and this, in turn results in a larger PL. A reduction of the spin-1/2 excitation also reduces the number of nonradiative recombination centers and thus also increases the PL.

If spin-1 (triplet) excitations are also present in the sample, a resonance at half of the magnetic field of the spin-1/2 resonance is expected. This triplet resonance should increase the luminescence [16]. Using PLDMR, we did not find within 1/100 of the $S=1/2$ signal any indication for the existence of triplet excitons in PDPA-nBu (Figure 2-(b)). As predicted by Takimoto [5], triplet excitations are unstable in polymers with a degenerate ground state. Thus our observation agrees with the expectation from theoretical models.

5. Ground state degeneracy in PDPA

Since disubstituted acetylene polymers like PDPA-nBu have a polyacetylene backbone, two equivalent dimerization patterns are possible in these materials. Thus the chemical structure already suggests that these materials have a degenerate ground state. Soliton excitation can only exist in degenerate ground state materials. Therefore the detection of solitons (in the following sections) in PDPA-nBu proves the hypothesis of degeneracy.

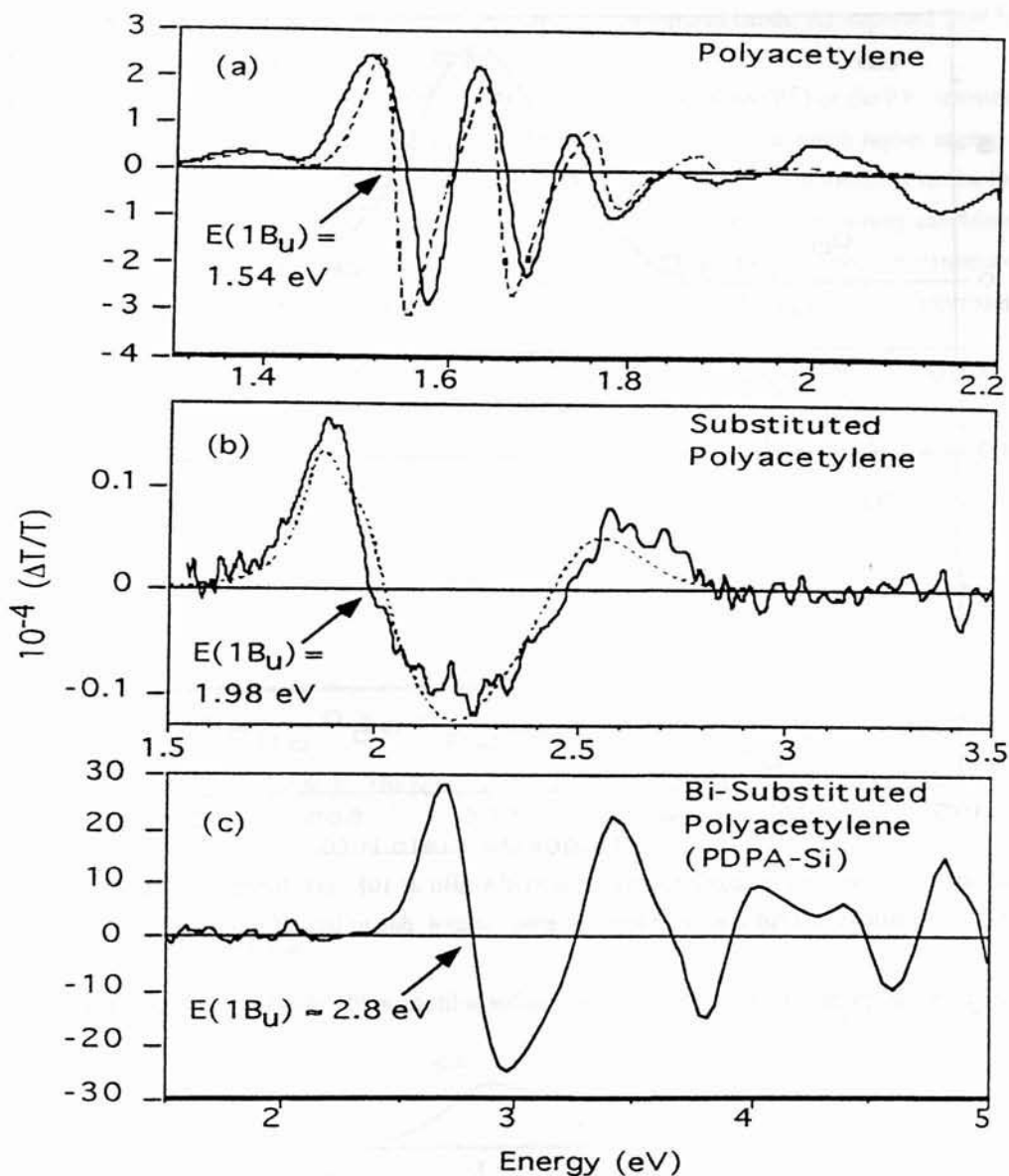


Figure 1: Electroabsorption spectra of different t-PA-derivatives. The energy level of the $1B_u$ exciton is indicated by the first prominent zero crossing. The dashed lines show the results of model calculations.

5.1 Doping experiments on PDPA-nBu

Infrared absorption spectra of doped π -conjugated polymers help to identify the nature of charged excitations with transitions below the gap. A film of PDPA-nBu was successively doped in iodine vapor. We define $\Delta\alpha d$ as the difference between the IR-absorption-spectrum of the doped material and the undoped material. For weak and strong doping levels $\Delta\alpha d(\omega)$ did not look qualitatively different. The differential absorption spectra $\Delta\alpha d(\omega)$ showed a pronounced doping induced band at 1.2 eV. A change in the phonon structure was also evident at 0.155 eV. This IRAV signature scaled together with the absorption band at 1.2 eV for different doping concentrations. This indicates that the absorption band is due to charged excitations [19]. Except for the IRAV signature, only one band appears due to doping. This suggests that this band is caused by charged solitons because polarons and polaron pairs have two absorption bands, and bipolarons will not appear at

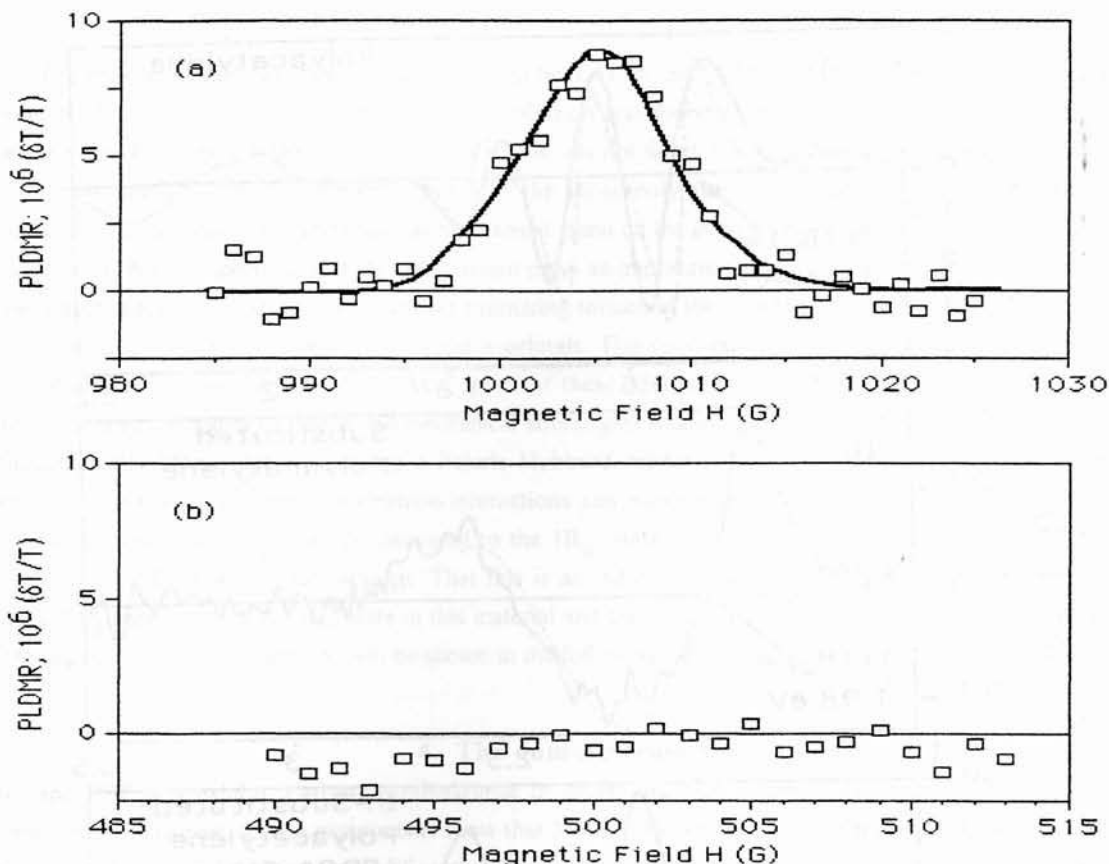


Figure 2: Photoluminescence detected magnetic resonance of PDPA-nBu at 10K. (a): Increased luminescence for $g=2$ due to resonance of spin-1/2 excitations. (b) No change in luminescence for $g=4$ due to lack of spin-1 excitations.

low doping levels. Thus the spectra show the existence of positive solitons in PDPA-nBu due to iodine doping according to the reaction



5.2 PA in PDPA-nBu

The PA spectrum of fresh PDPA-nBu (Figure 3) reveals a new band, peaking at 1.7 eV, at an energy above that of the S^+ band which appears due to iodine doping. Neutral solitons have a single absorption band at higher energies compared to that of charged solitons [14]. The band at 1.7 eV must be then either due to neutral solitons, or to triplets. PLDMR demonstrates that triplet excitons do not occur in PDPA-nBu. We will show below by PADMR that the band at 1.7 eV can be assigned to neutral solitons (S^0).

For PA measurements on films with a high concentration of defects, photooxidized films were prepared by exposing the film for two hours to 0.1 W/cm^2 at 458.9 nm laser light illumination at room temperature in air. PA measurements on photooxidized films show not only the characteristic transitions of S^{\pm} and S^0 known from doping and PA of fresh films, but in addition a third band at 0.3 eV also appears (Figure 4(b)). The pump intensity, frequency and sample quality dependence

of the infrared bands was measured to examine the possible correlation of the infrared bands. As expected from theory, the S^0 band at 1.7 eV does not correlate with either of the low energy PA bands.

The new band at 0.3 eV can only be assigned to the P_1 transition of polarons (P^\pm) or the PP_1 transition of polaron pairs (PP). Also exclusion leads to the same result: Triplet transitions should be found at much higher energy and were not found in this sample using PLDMR measurements. Solitonic transitions have already been assigned to the band at 1.7 eV (S^0) and at 1.1 eV (S^\pm). They are also at higher energies, closer to the mid gap. The only remaining candidate for the low-energy PA band are P_1 and PP_1 . The existence of the transition P_1 or PP_1 implies the respective transition P_2 or PP_2 . The respective transitions are located symmetrically about the midgap energy. Since the bandgap is at approximately at 2.8

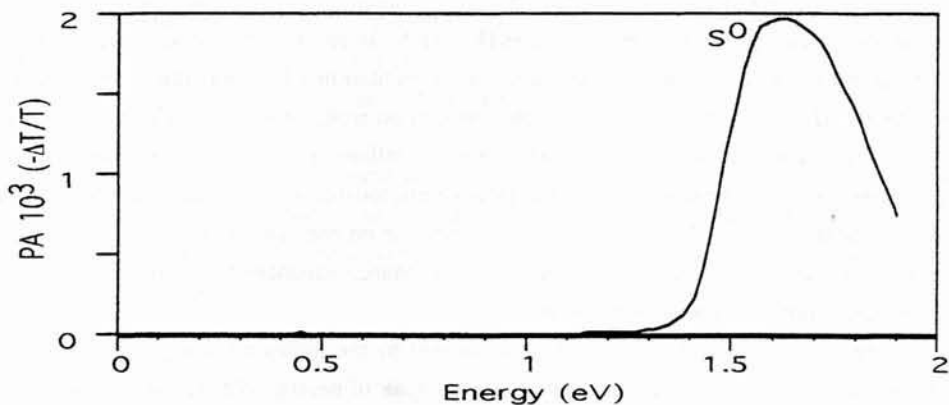


Figure 3: PA of a fresh PDPA-nBu film at 80 K. The pump is the 458.9 nm line of an Ar⁺ laser.

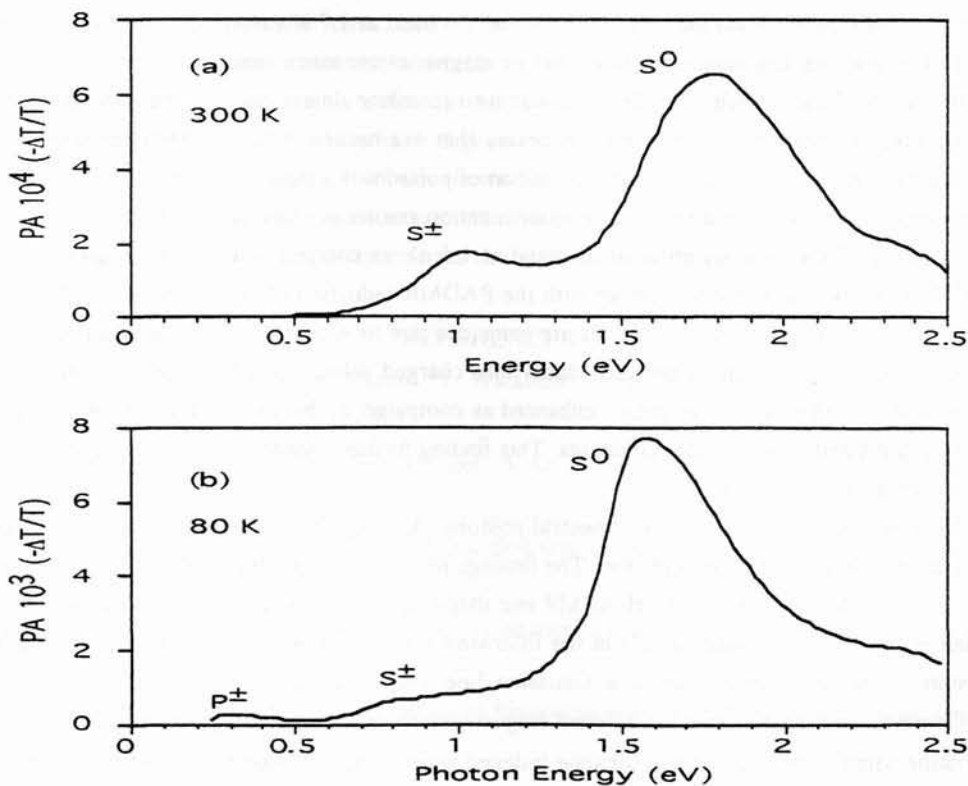


Figure 4: PA of a photooxidized PDPA-nBu film at room temperature and at 80K.

eV, the transition P_2 or PP_2 should be located roughly around 2.5 eV. Figure 4(b) shows a shoulder of the PA at around 2.5 eV which might account for the P_2 or PP_2 transition. Since polarons and polaron pairs are closely related, the band at 0.3 eV is labeled P^\pm .

5.3 PADMR of PDPA-nBu

PADMR is an efficient technique to confirm the findings from PL, PLDMR, doping and PA measurements. To assemble spectra that supply detailed information of the magnetic resonance over a wide range of photon energies, H-PADMR has been measured at 10 K at different probe wavelengths. The data (Figure 5) fit well the sum of a narrow Lorentzian (FWHM = 15 G) and a broad Gaussian function (FWHM = 56 G). The amplitudes of the narrow and the broad functions are plotted versus the probe photon energy for 3 different samples (Figure 5). In all samples, the resulting λ -PADMR spectrum of PDPA-nBu shows the magnetic resonance induced generation of an excitation which was identified as charged soliton by doping experiments. The λ -PADMR spectrum shows also bleaching of polarons between 0.3 eV and 0.7 eV and bleaching of neutral solitons above 1.5 eV. The sample quality has an important influence on the magnetic resonance width and the relative strength of the three PADMR spectral features: Progressive photooxidation enhances the PADMR signatures at 0.3 and 1.1 eV with respect to the feature at 1.7 eV. The similar dependence on the sample quality suggests that the bleaching and absorption bands at 0.3 eV and 1.1 eV are related: Magnetic resonance enhances the conversion of excitations with an absorption at 0.3 eV into excitations with an absorption at 1.1 eV.

The previous given assignment of the three bands is supported by the following interpretation of the PADMR data: For neutral solitons to recombine, they must have opposite spins. If a pair of neutral solitons has parallel spins, they can not recombine unless one of the spins changes its direction. A spin flip can occur due to electron lattice interaction or due to magnetic resonance. Thus magnetic resonance enhances the recombination rate of neutral solitons with parallel spin on the polymer chain. This confirms the previous interpretation that the PA band at 1.7 is a result of transitions of neutral solitons. Likewise the effect of mixing the spin quantum states due to magnetic resonance enhances the recombination process of polarons with parallel spins: Polarons with parallel spins cannot recombine unless one of them changes its spin direction. Magnetic resonance greatly enhances the spin flip processes that are necessary for polaron recombination. Thus the interpretation that the band at 0.3 eV is due to the P_1 transition of polarons is supported by the PADMR data.

If two polarons are of the same charge, their recombination results in charged solitons in degenerate ground state conjugated polymers [4, 7]. Thus the assignment of the band at 1.1 eV as charged soliton transitions is also supported by the fact that its PADMR enhancement scales together with the PADMR reduction of the polarons in different samples. The interpretation is supported by the fact that these bands are enhanced due to successive photodegradation, as can be seen in Figure 3 and Figure 4. Following excitation, polarons decay into charged solitons and therefore in a photooxidized sample the bands of charged solitons and polarons are greatly enhanced as compared to the photoinduced neutral soliton absorption. This can be seen in both PA and PADMR measurements. This finding further confirms the interpretation of the various PA and PADMR bands mentioned previously.

Some of the defects occur as free radicals or neutral solitons. As suggested by Orenstein *et al.* [9] these defects can directly be charged due to the absorption of a photon. The findings presented in this study agree with this model.

We can understand the evolution of the H-ADMR line shape from mainly a narrow Lorentzian in the pristine sample to a broad Gaussian in the photo oxidized sample in the following way: A Lorentzian line shape is associated with three-dimensional diffusion of the spin carriers, while a Gaussian line shape indicates trapped immobile spins [29]. The broadening of the Gaussian function indicates the different magnetic environment of the trapped spins.

In the pristine sample the magnetic resonance induced quenching of polarons (0.2 eV - 0.6 eV) has a purely Lorentzian line shape (Figure 5 (a)). This is an indication, that polarons move freely in this sample. In the weakly photo

oxidized sample, the H-ADMR signal for polarons is composed of a Gaussian and a Lorentzian line shape (Figure 5 (b)). This indicates that some of the polarons are mobile while others are trapped in defects. When the sample is further photo oxidized (Figure 5 (c)), all polarons are trapped.

Charged solitons do not carry spin and therefore they are not directly detected by magnetic resonance. Thus the signal between 0.7 eV and 1.5 eV indicates the magnetic resonance induced generation of charged solitons due to an indirect process such as the resonance induced conversion of a spin-1/2 species into charges solitons. Possible candidates are only polarons and neutral solitons, which both are quenched by magnetic resonance. Since their generation is indirect, the H-ADMR line shape of charged solitons replicates the line shape of the generating species. The H-ADMR signal of the pristine sample indicates clearly, that charges solitons are generated by polarons. This generation process is enhanced by the magnetic resonance of polarons. Magnetic resonance does not enhance the conversion of neutral solitons into charged solitons. This becomes evident since the neutral soliton signature is composed of a signal of free and trapped spins, while the signature of charged solitons and of polarons indicates that these particles are mobile in the pristine film. This result is in agreement with the previous discussion.

As expected, a higher level of photooxidation successively traps all photoexcitations in the material. In the pristine material, polarons and charge solitons are mobile, while neutral solitons exist trapped and mobile as well. We speculate that the trapped neutral solitons are a result of the chemical synthesis process while the mobile solitons are the decay product of triplet excitons in the defect free material.

6 Conclusions

Disubstituted polyacetylene, PDPA-nBu, is a material that supports excitons, solitons, and polarons. The primary photoexcitations in this polymer are the odd parity singlet $1B_u^1$ excitons. Since the triplet level $1B_u^3$ is unstable towards formation of two neutral solitons with parallel spins, inter system crossing of $1B_u^1$ into $1B_u^3$ leads to the generation of pairs of neutral solitons with parallel spin, which can be detected with magnetic resonance. Defects in the material lead to an enhanced number of charged excitations, namely polarons and charged solitons. Solitons can only exist in a degenerate ground state conjugated polymers, thus PDPA-nBu has a degenerate ground state. In this study, the existence of excitons in a degenerate ground state π -conjugated polymers has been shown for the first time. We speculate that the luminescence of PDPA-nBu is a result of relatively weak electron-electron interaction compared to other interaction which determine the gap. This is a result of the large sidegroups. Figure 6 summarizes the quantitative results of the measurements in PDPA-nBu.

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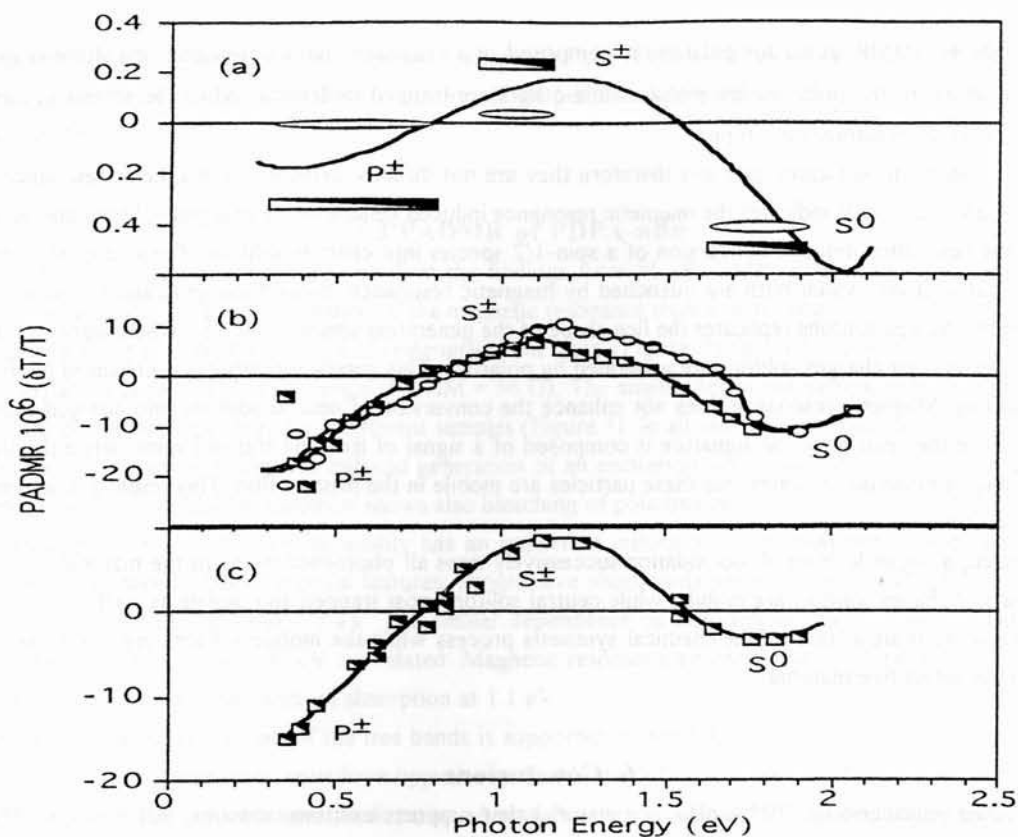


Figure 5: λ -PADMR spectra of different films of PDPA-nBu. (a): A pristine film. (b): The film is slightly photo oxidized during handling. (c): The film is photooxidized with 0.1 W/cm^2 of 458.9 nm for 2 hours at room temperature. Squares and rectangles represent the narrow component of the magnetic resonance (FWHM = 15G) whereas the circles and ovals represent the broad component (FWHM = 56G). The solid lines serve as a guide to the eyes.

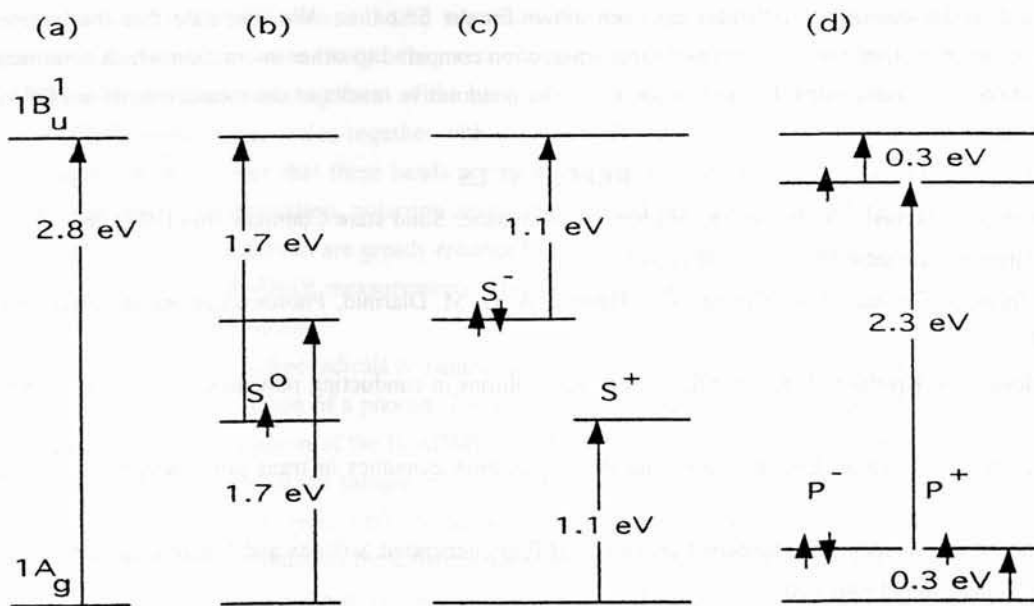


Figure 6: The optical gap of PDPA-nBu (a) in comparison with neutral (b) and charged (c) solitons and polarons (d).

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